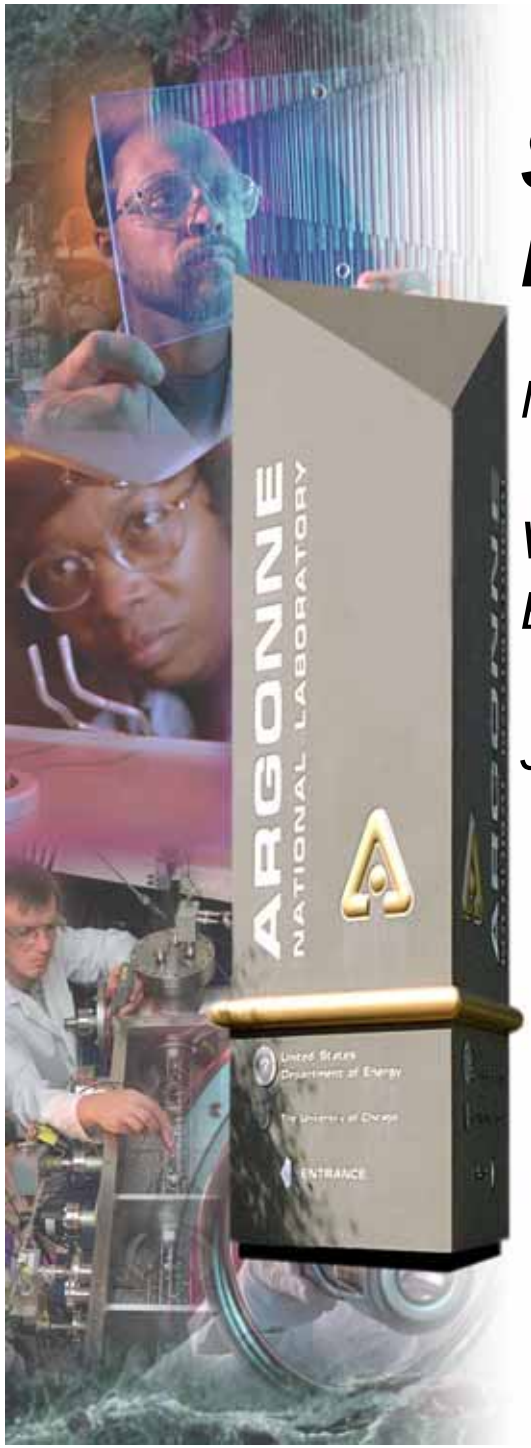


Separations of Actinide Elements

Monica C. Regalbuto

Workshop for Graduate Students from the Big 10 Nuclear Engineering Departments

July 20-22, 2004

Argonne National Laboratory

Office of Science
U.S. Department of Energy

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

Actinide Separations

- **Why are they needed?**
  - Can address major technical, social and political issues related to disposal of nuclear wastes
  - Regulatory requirements associated with actinide waste disposal are more stringent than those for other radioactive wastes
    - *Waste present a greater health hazard*
    - *Isotopes have long half lives*

- **Sources of actinides**
  - “Legacy waste” from weapons production
  - Spent nuclear fuel
  - Medical and industrial isotope production wastes

Actinides Are Separated from What?

- **Mainly from**
  - Each other

Actinide Series~	90 Th 232.0	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)

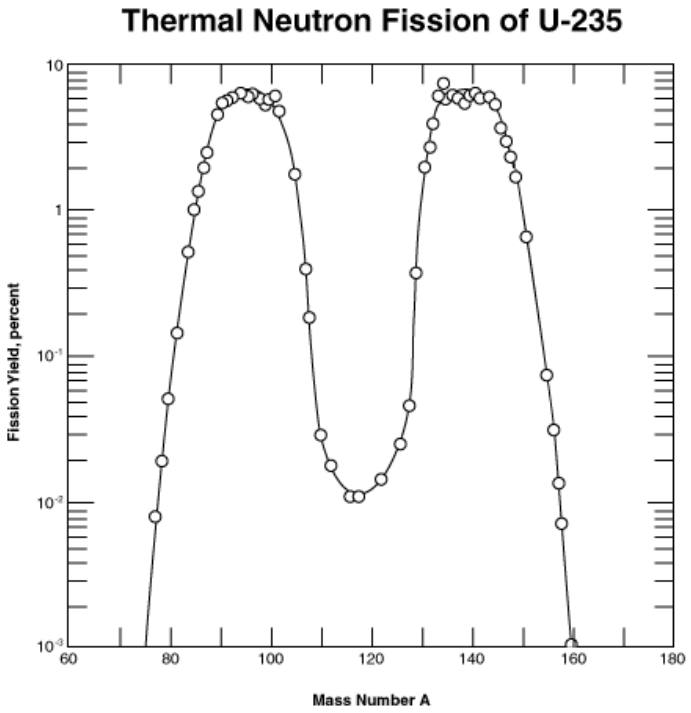
  - Lanthanides (also known as Rare Earths)

Lanthanide Series*	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
Actinide Series~	90 Th 232.0	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)

Actinides Are Separated from What?

- From other fission products

  Fission products with mass numbers around 90 and 140 have particularly high fission yields



5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La* 138.9														

What are the Actinides of Most Interest?

- **Those with a low atomic-number**
  - Elements beyond Cm are present in very low concentrations
    - *Produced only under highly specialized circumstances*

- **Those that are alpha-emitters**
  - Radium and radon are decay daughters of actinides

Isotope	Atomic No.	Half Life
Ra-226	88	1.6E+03 y
Rn-222	86	3.83 d

Isotope	Atomic No.	Half Life
U-232	92	69.8 y
U-233		1.59E+05 y
U-234		2.46E+05 y
U-235		7.04E+08 y
U-238		4.47E+09 y
Np-237	93	2.14E+06 y
Pu-238	94	87.7 y
Pu-239		2.41E+05 y
Pu-240		6.56E+03 y
Pu-242		3.74E+05 y
Am-241	95	4432.7 y
Am-242m		141 y
Am-243		7.36E+03 y
Cm-243	96	30 y
Cm-244		18.1 y
Cm-245		8.5E+03 y
Cm-246		4.73E+03 y

Non-technical Issues Associated with Actinide Separations

- **Primary applications are nuclear power generation and weapons production**
  - Because the technology can be applied to the production of weapons strict controls are imposed due to proliferation risks
    - *Material accountability*
    - *Safeguards and security*
  - From an R&D perspective these controls add a layer of complexity that does not exist in other separation applications

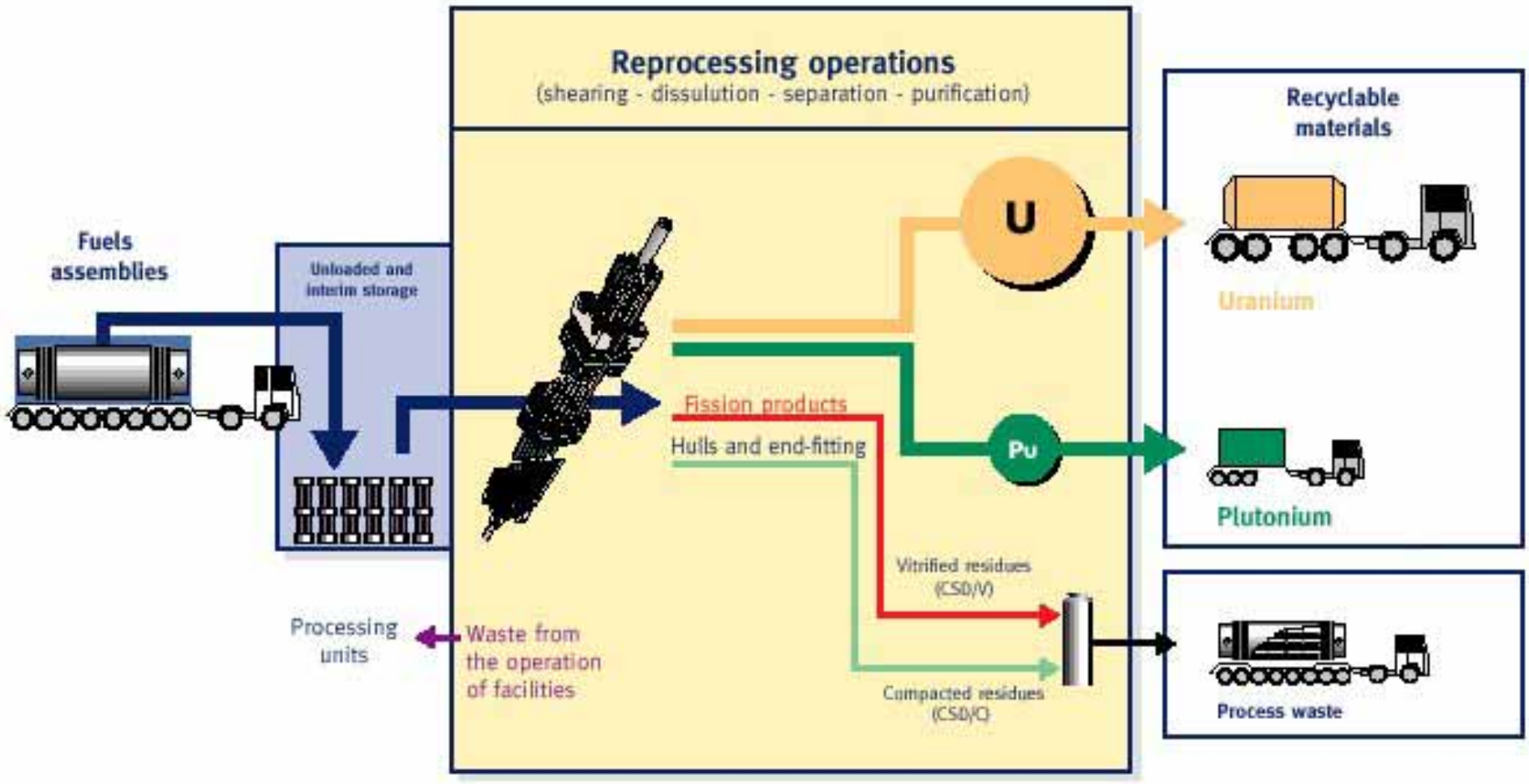
Technical Challenges to Actinide Separations

- **Concentrations in either spent fuel or in tank HLW will vary widely**
  - Must design separation processes robust enough for a wide range of feeds
  - Feed characterization requires significant analytic capability
- **Concentrations in feeds are very dilute**
  - Low concentrations in spent fuel (except for U)
  - Early nuclear area waste management approach was based on dilution and dispersal
- **Chemistry of actinides is complex**
  - Actinides form multiple valence states
  - Similar to that of lanthanides

State of the Art in Actinide Separation

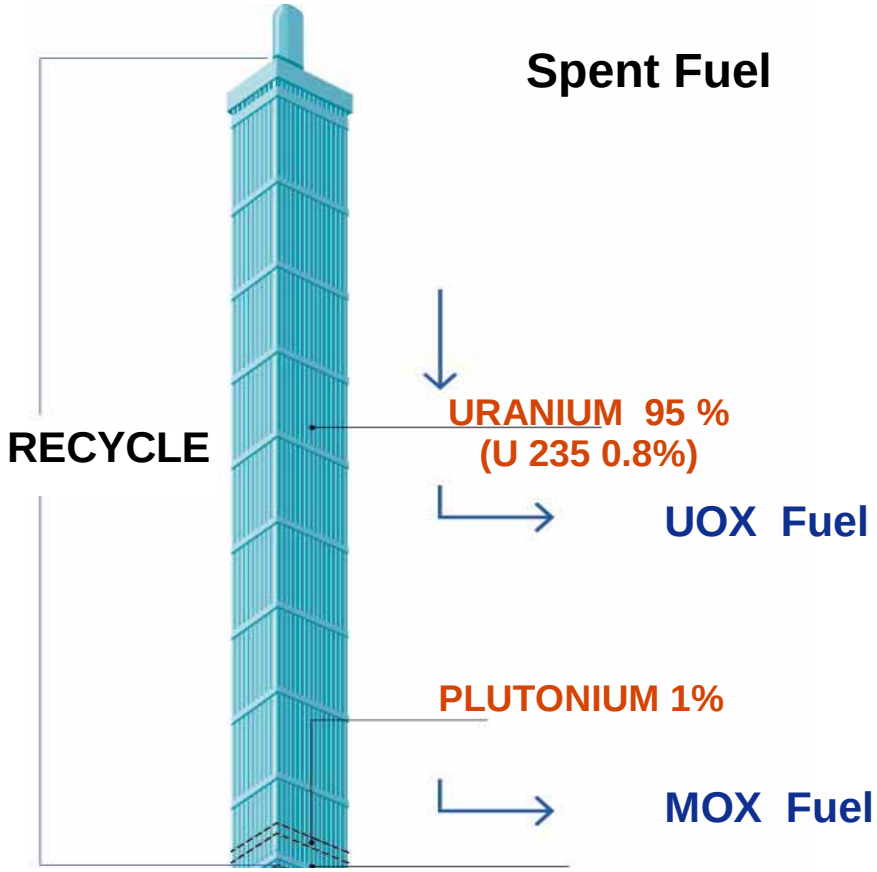
- **Aqueous based processes**
  - **Liquid-liquid extraction**
  - Precipitation
  - Ion exchange
  - Membranes
  - Crystallization
  - Supercritical fluid extraction
- **Dry processes**
  - **Pyroprocessing**
    - ***Electrorefining***
    - ***Oxide reduction***
  - Volatilization
- **Others**

Actinide Separation – Fuel Cycle



Slide courtesy of COGEMA

Spent Fuel Contains 96% Recyclables



Slide courtesy of COGEMA

Actinide Separations Capabilities at ANL

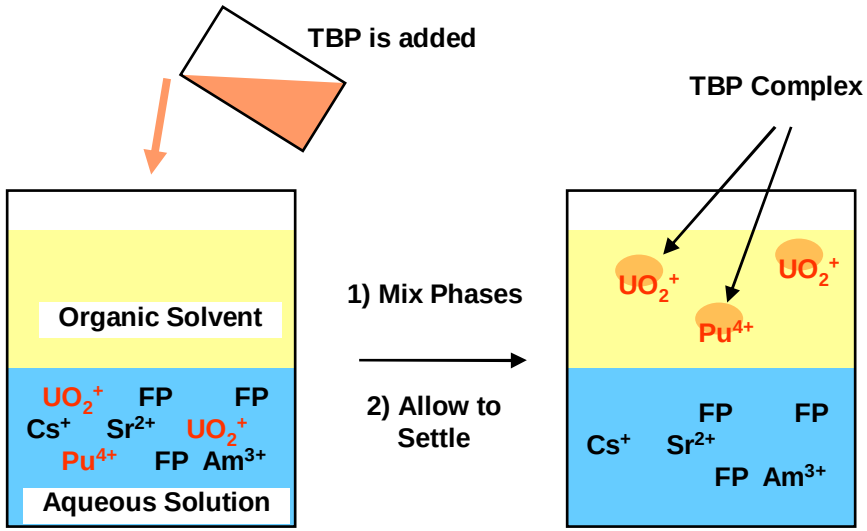
ANL research on actinide separations dates back to the late 1940s

- **Liquid-liquid extraction**
- **Pyrochemical processing**
- **Spent fuel treatment**
- **TRU, high and low-level waste treatment**
- **Trace analysis of radionuclides**

Liquid-liquid Extraction

Solvent Extraction Principle

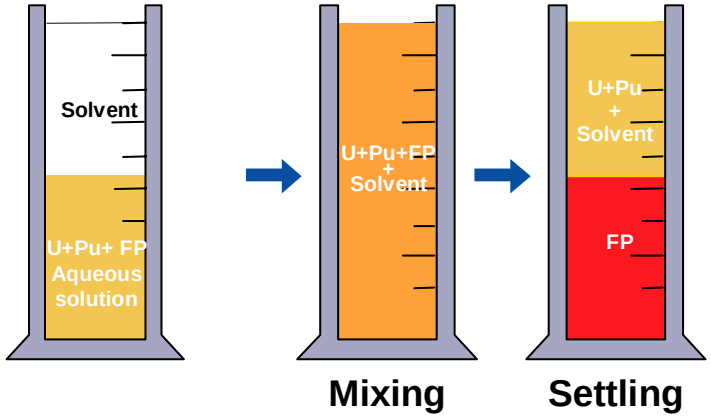
- **Based on relative stability of a metal species in two immiscible liquids**
  - The metal to be separated is contacted with both liquids and is partitioned into each at a constant ratio (the distribution coefficient)
- **Multiple extractions**
  - Not always possible to remove 100% metal with one contact.
  - Options are to greatly increase amount of solvent volume or to use multiple contacts



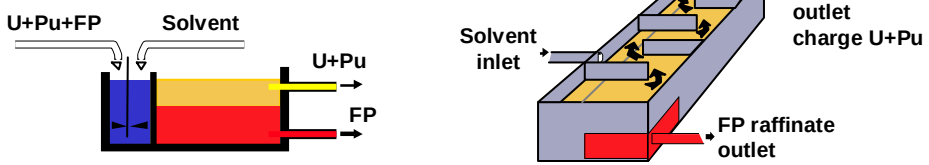
Solvent Extraction Equipment

- **Centrifugal Contactors**
  - Short residence time protects solvent from radiolysis and hydrolysis degradation
  - High efficiency
  - High throughput
  - Step-wise phase contact
  - Compact unit
  - Quickly reaches steady state
- **Mixer-settlers**
  - Long residence time
  - Step-wise phase contact
  - Extraction combined with reaction
- **Pulsed Columns**
  - Long time to reach steady state
  - Products with low density difference, low interfacial tension or having a tendency to form emulsions
  - High throughput

Solvent Extraction Equipment

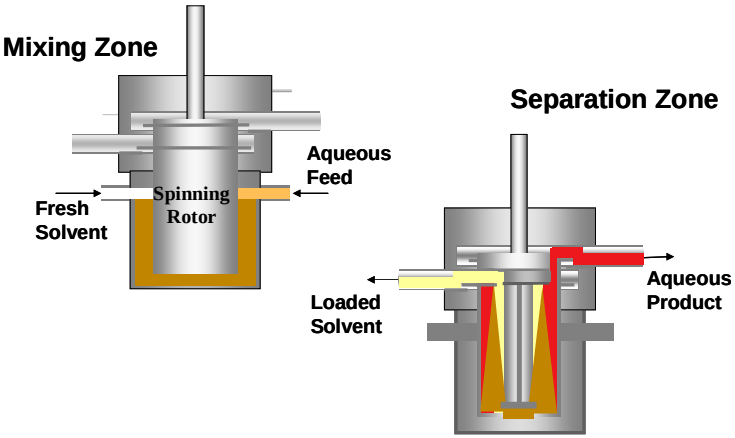


Mixer-settler

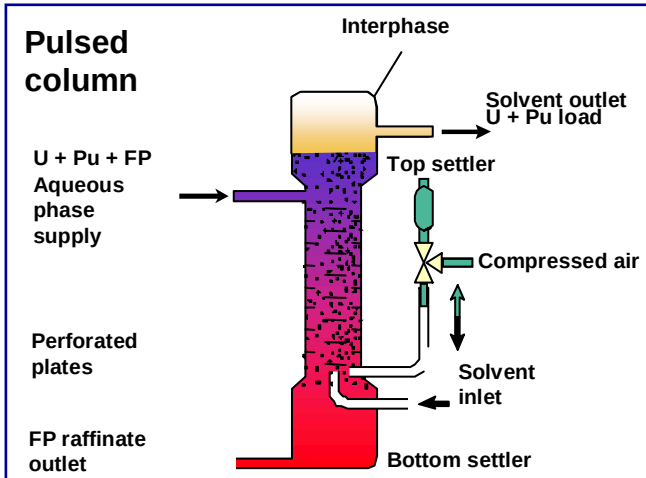


Figures courtesy of ANL and COGEMA

Centrifugal Contactor



Pulsed column

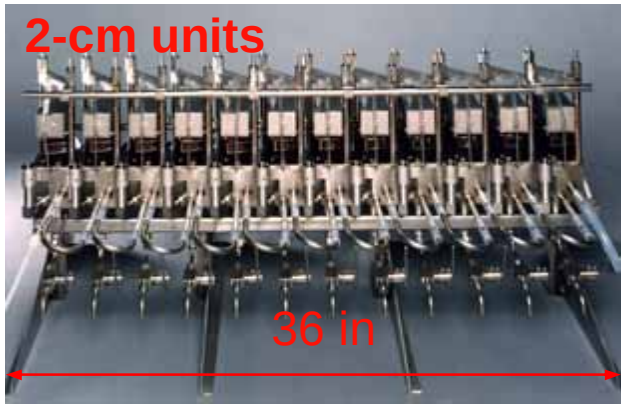


ANL Solvent Extraction Expertise

- **Equipment design**
- **Process modeling and design**
- **Process demonstration**

Equipment Design - ANL Centrifugal Contactor

Pilot-scale Centrifugal Contactors

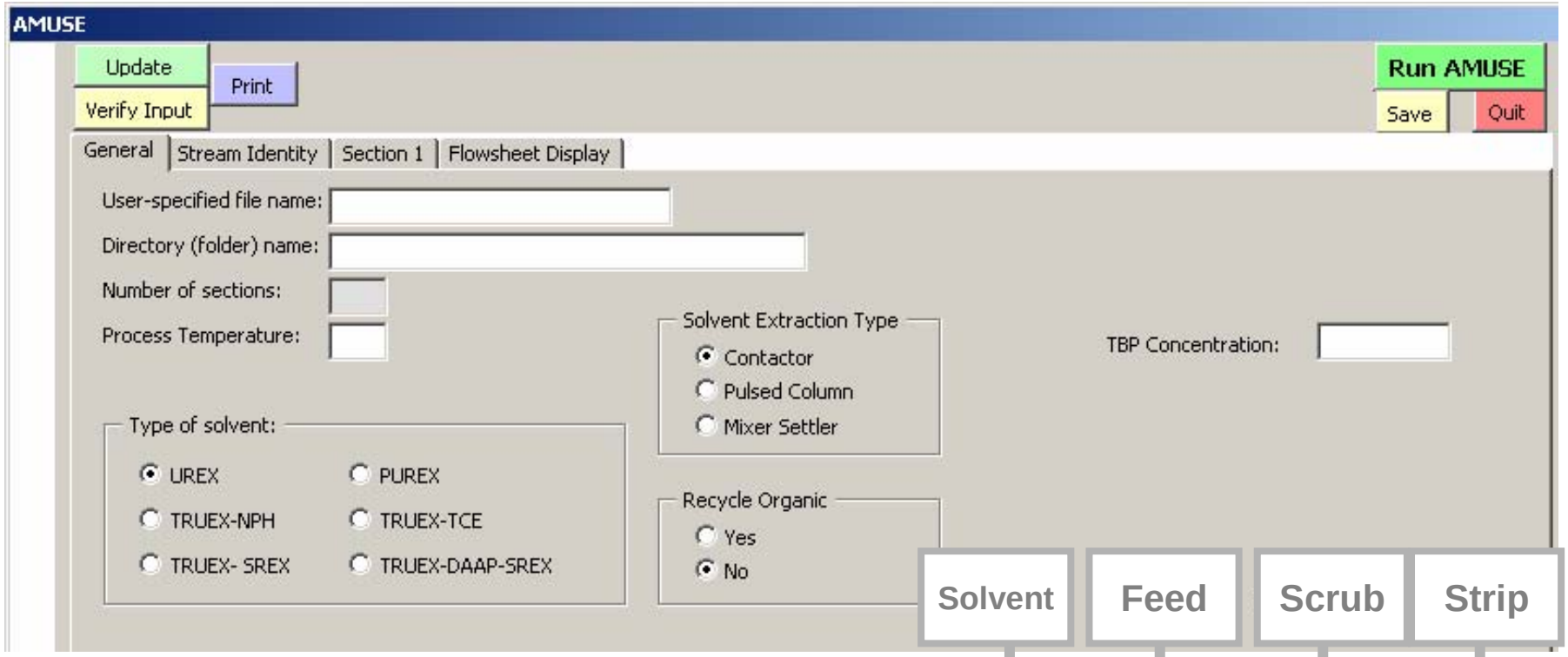


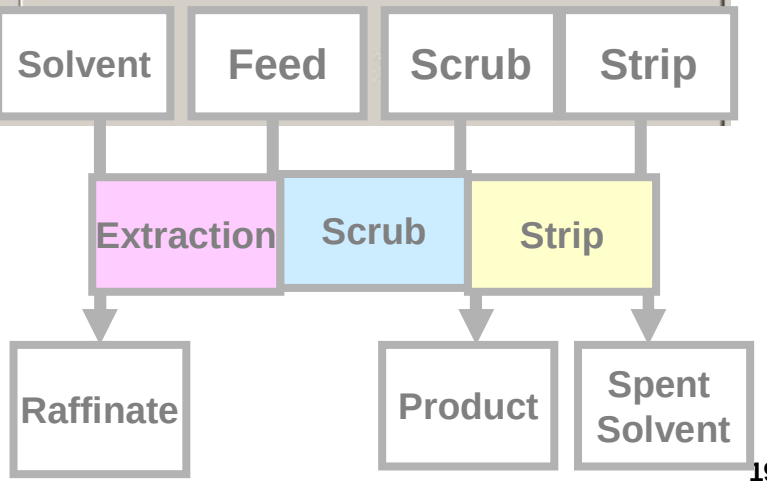
Rotor Diameter cm	Nominal Throughput L/min
2	0.04
4	0.4
9	10
10	12 → 0.65 t/d
12	20
25	120

Process Design and Modeling - AMUSE

- **The Argonne Model for Universal Solvent Extraction—AMUSE is a tool we use to:**
  - Design and optimize solvent extraction flowsheets
    - *PUREX, UREX, TRUEX, SREX*
  - Perform sensitivity analysis to determine key process variables and their control bound
    - *Flow rates, number of stages, concentration of feed components, concentration of solvent, temperature*

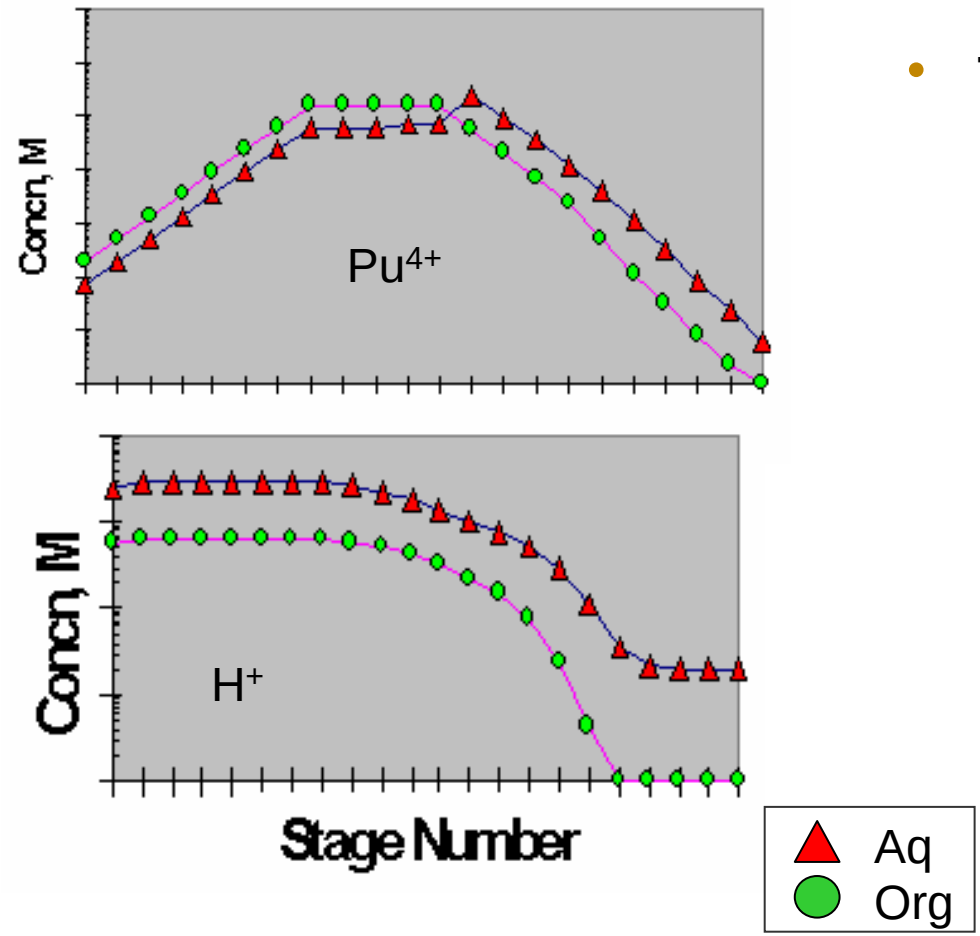
AMUSE - General Input Form





AMUSE – Results

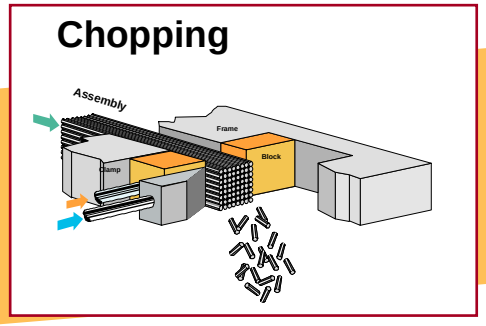
GRAPHICAL

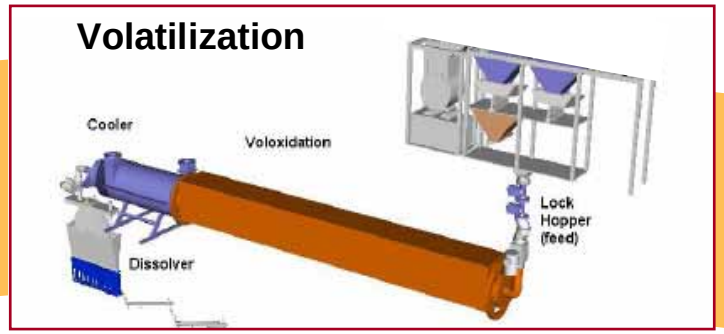


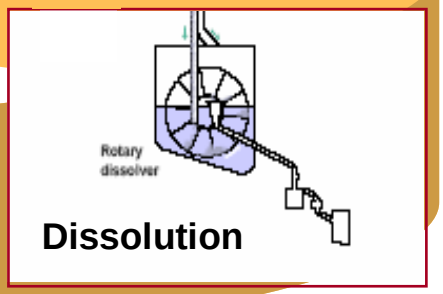
TABULAR

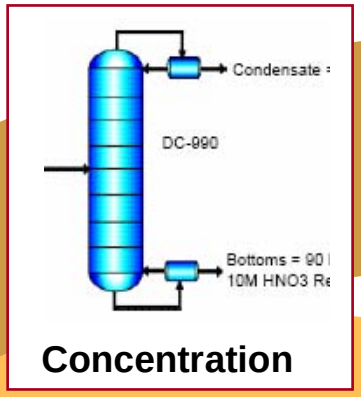
- **Tabular reports are created for**
  - Influent and effluent compositions and flow rates
  - Stage profiles that include
    - *Distribution ratios*
    - *Component concentrations in organic and aqueous phases*

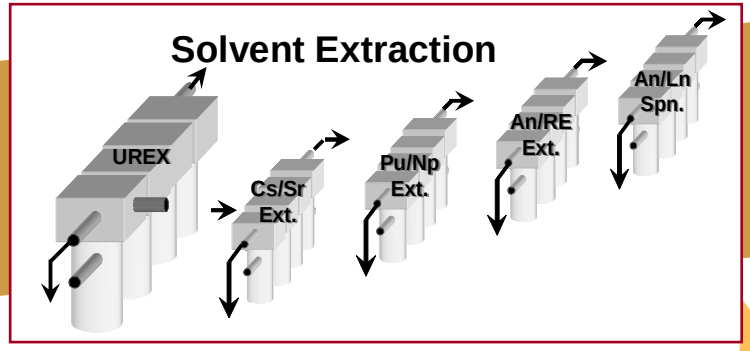
Aqueous Spent Fuel Treatment Facility

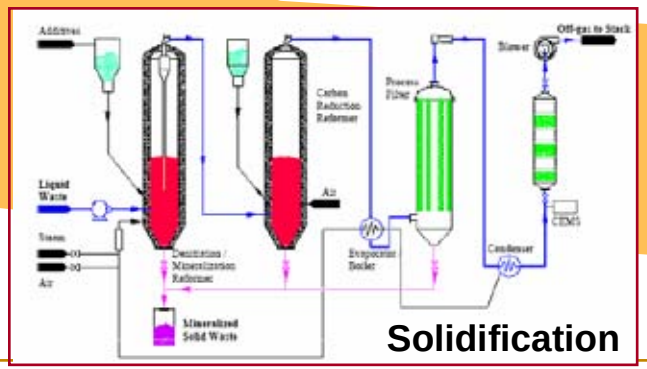


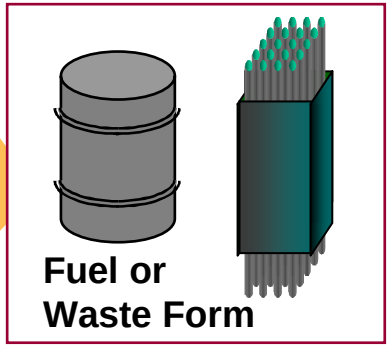












Figures courtesy of ANL
WGI and COGEMA

Process Demonstration – UREX+

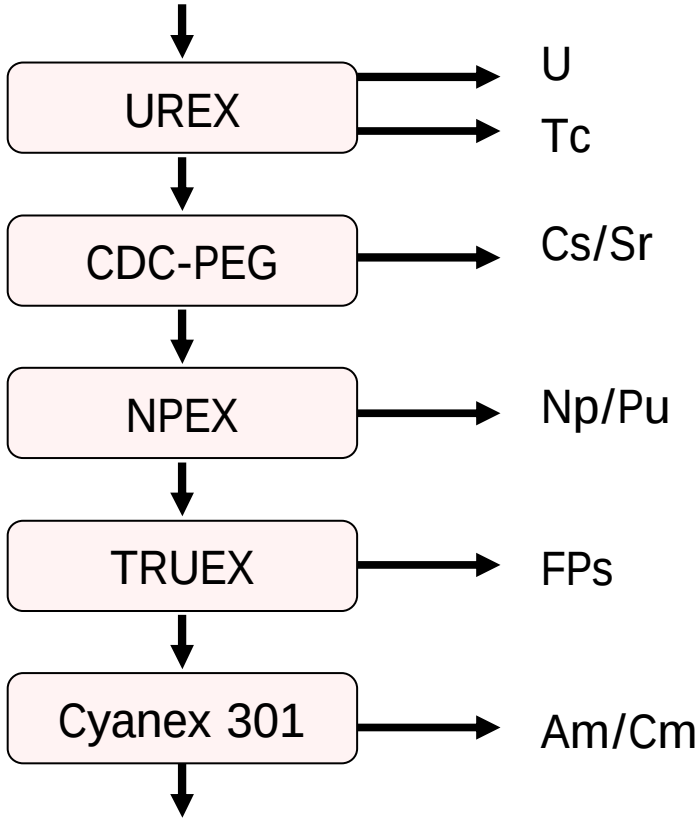
- **Process being developed as part of the Advanced Fuel Cycle Initiative (AFCI)**
- **Objective:**
  - Demonstrate that all desired spent fuel constituents can be separated to meet required specifications by aqueous processing
- **ANL work is centered on process design, modeling, and demonstration**

Process Demonstration – UREX+

- **Spent fuel dissolution**
- **Aqueous based separations:**
  - A series of five solvent-extraction process which separates spent fuel into six product and waste streams
    - U_3O_8 for recycle or disposal as LLW
    - Np/Pu for mixed oxide fuel for thermal reactors
    - Tc and I for immobilization as HLW
    - Am/Cm for fast-reactor fuel
    - Cs/Sr for decay storage
    - Mixed fission products for repository disposal

Process Demonstration – UREX+

- **Flowsheets**
  - Developed using the AMUSE code
- **Equipment**
  - Three ANL-designed 2-cm contactors were used, set up in a shielded cell, a glovebox, and a vacuum-frame hood
  - Can process ~2 kg/day spent fuel (heavy metal)

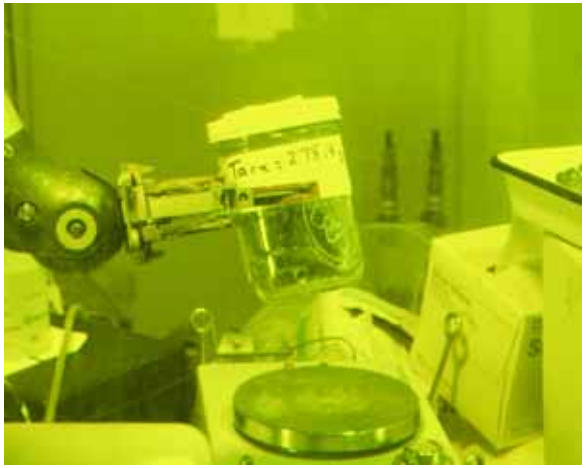


Process Demonstration – UREX+ Spent Fuel Dissolution

ANL-designed 2.25 L

304L SS pressure vessel

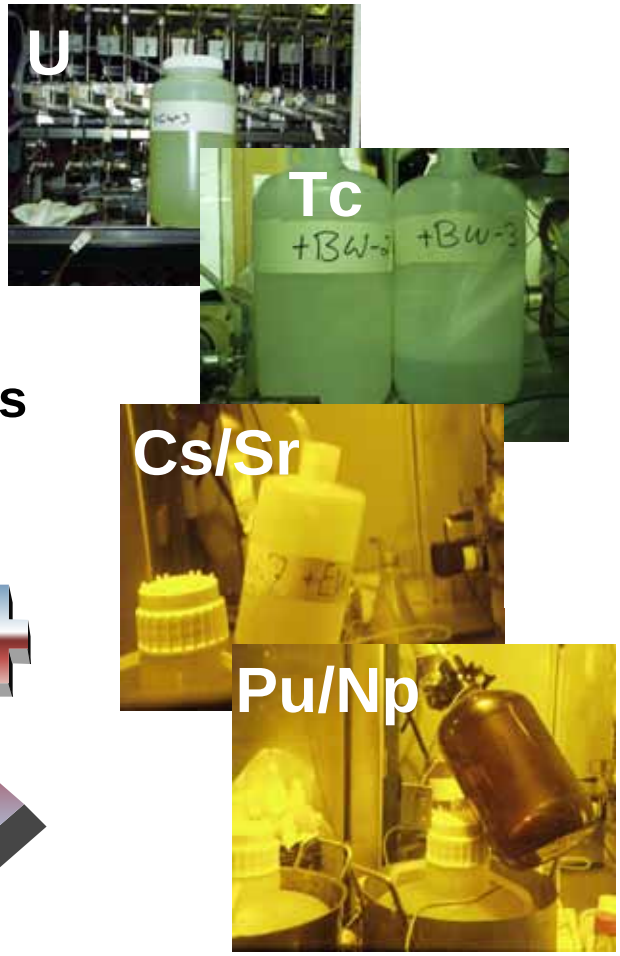
- **UO_2 was completely dissolved**
- **Cladding hulls were very clean**
- **Sludge was minimal and easily filtered**
- **Solution was stable**



Process Demonstration – UREX+ Results

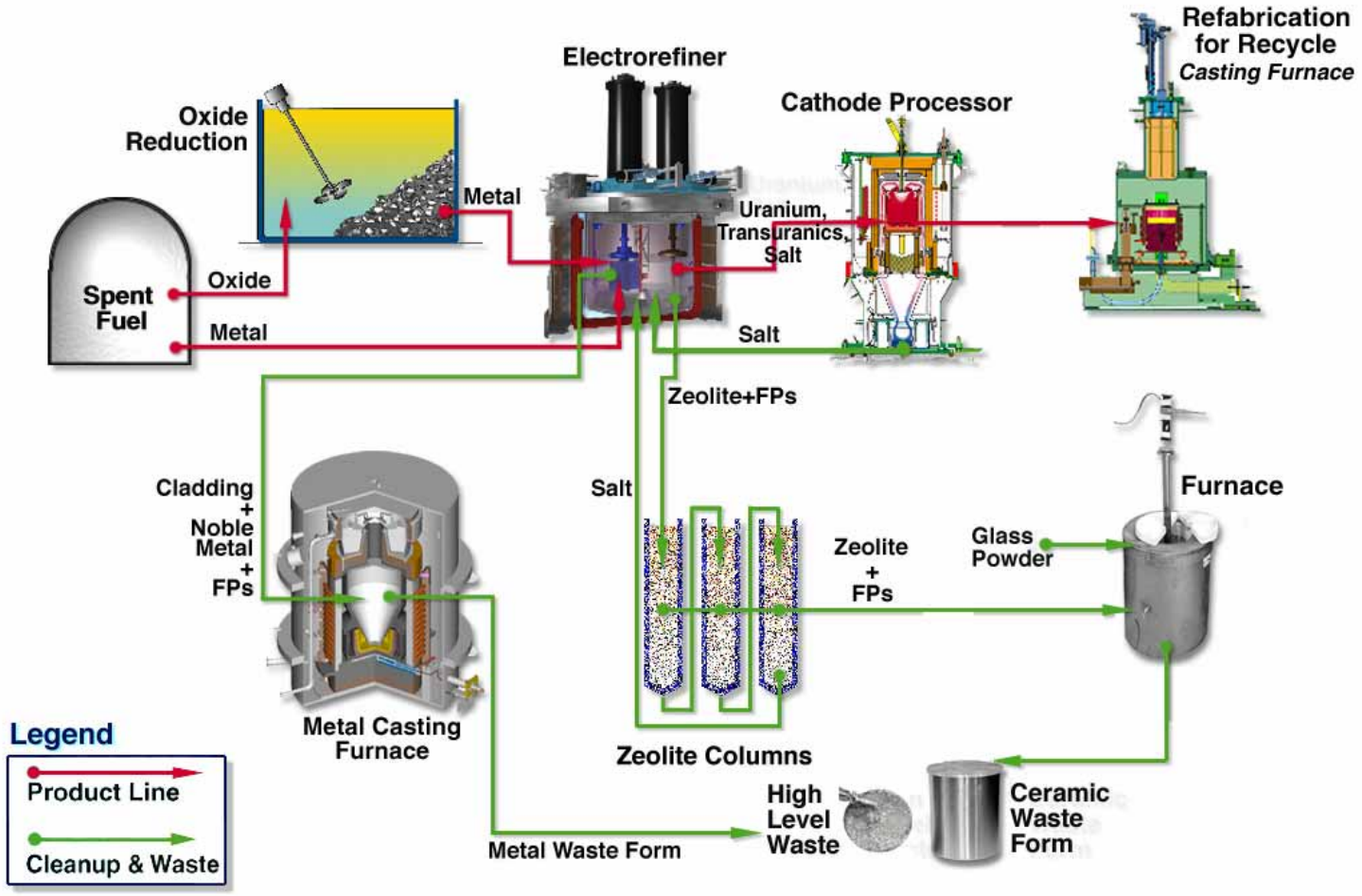
- **All processes show high promise for meeting process goals**
  - Disposal of uranium as class C LLW
  - Technetium fissile content
  - Pu/Np MOX fuel fabrication
  - Disposal of Cs/Sr as LLW
- **Excellent selectivity for the desired products demonstrated for all processes**

UREX+



Pyroprocessing

Pyroprocessing Oxide Fuel



Oxide Reduction Process

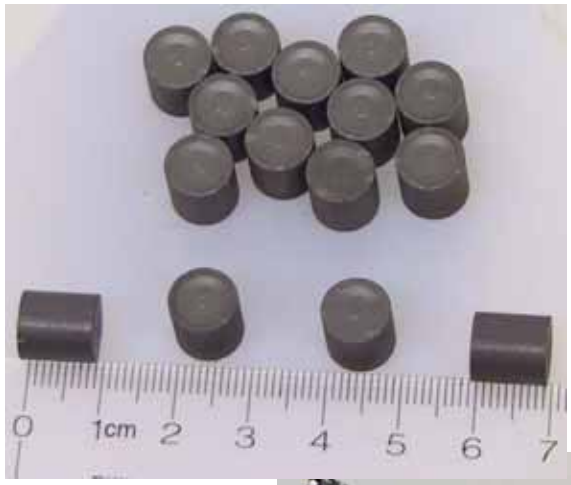
- **Goal - develop a commercially viable process for reducing spent fuel oxides to metals**
  - **High product quality**
  - **High throughput**
  - **Simple engineering**

- **Cathode process**

  MO_X (s) + 2xe^- = M (s) + x O^{2-}

- **Anode process**

  2 O^{2-} = O_2 (g) + 4 e^-

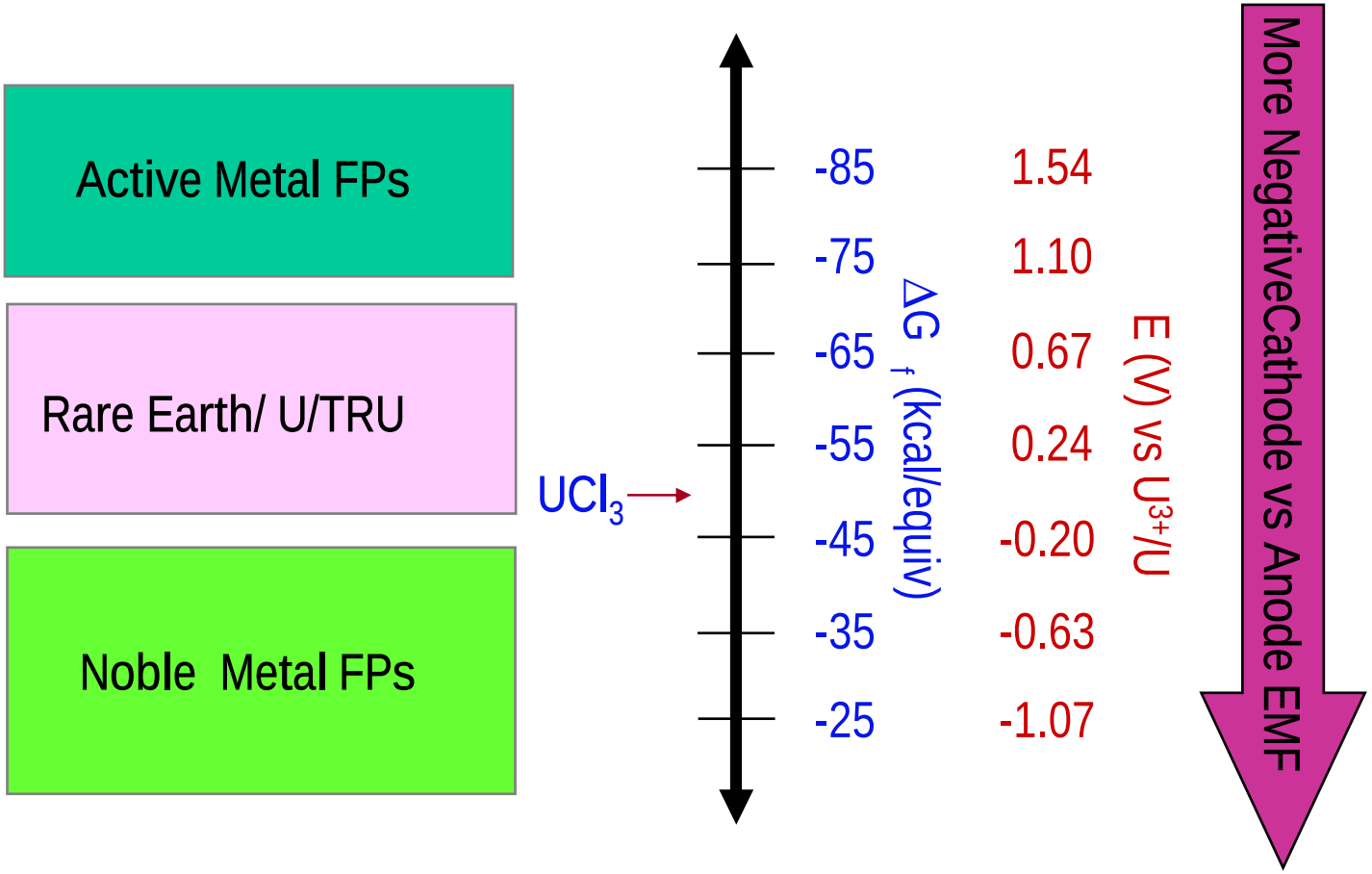


Oxide Reduction Cell and Product

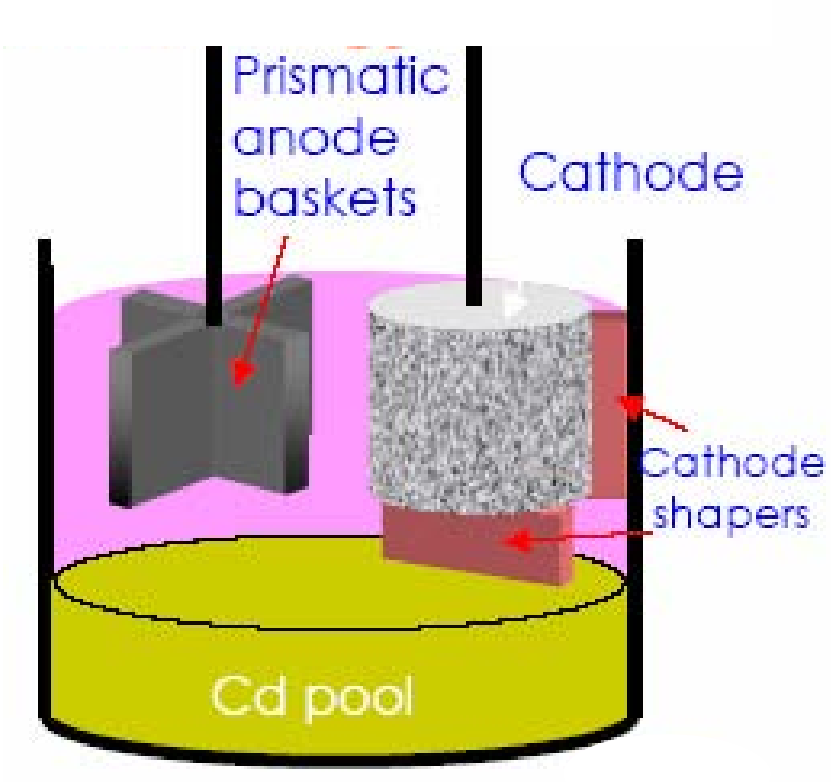
Why Electrorefine Uranium

- **Separate uranium from spent nuclear fuel for recycle or disposal as LLW**
  - EBR-II (metal)
  - LWR fuel (oxide)

Thermodynamic Basis



Pyroprocessing Equipment - Electrorefiner



Engineering-Scale Electrorefiner

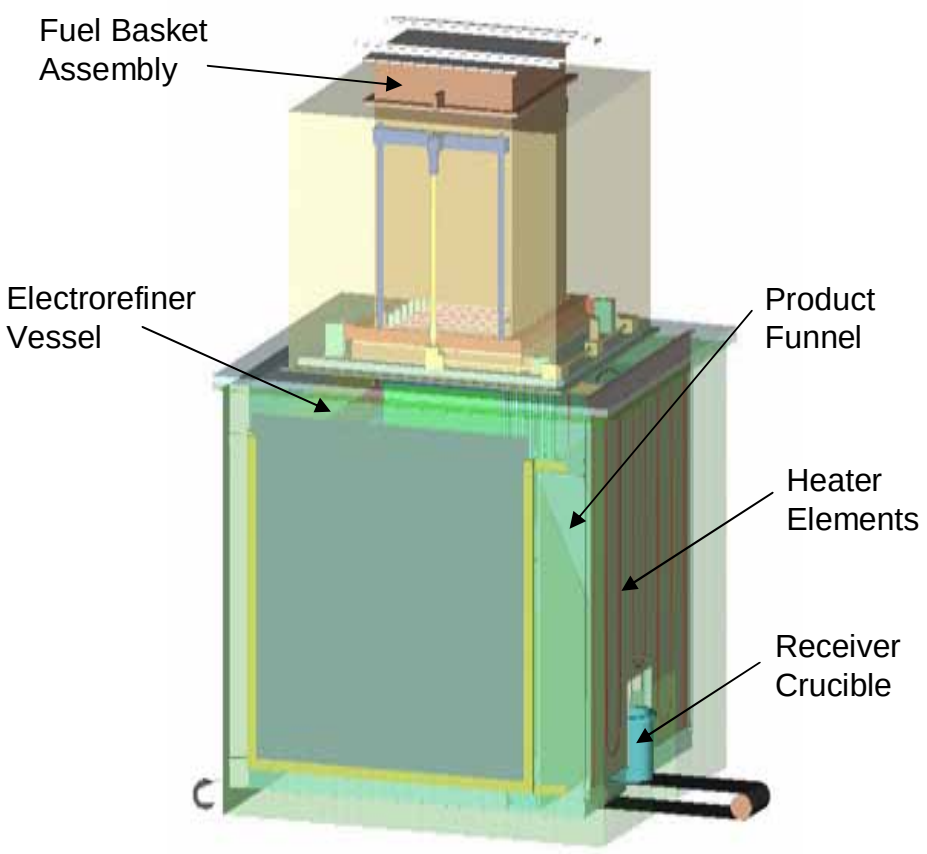
Mk-V ACM - Anode Assembly

ANL Pyroprocessing Expertise

- **Equipment design**
- **Process modeling and design**
- **Process demonstration**

Equipment Design

- High throughput electrorefiner
- Electrolytic oxide reduction
- Pyro-contactors
- Liquid cadmium cathode
- Cathode processor
- Metal waste form casting furnace
- Pressureless consolidation for ceramic waste forms



High Throughput Electrorefiner Prototype

Process Design

Integration of unit operations to provide an economical recycle process for commercial oxide fuel treatment

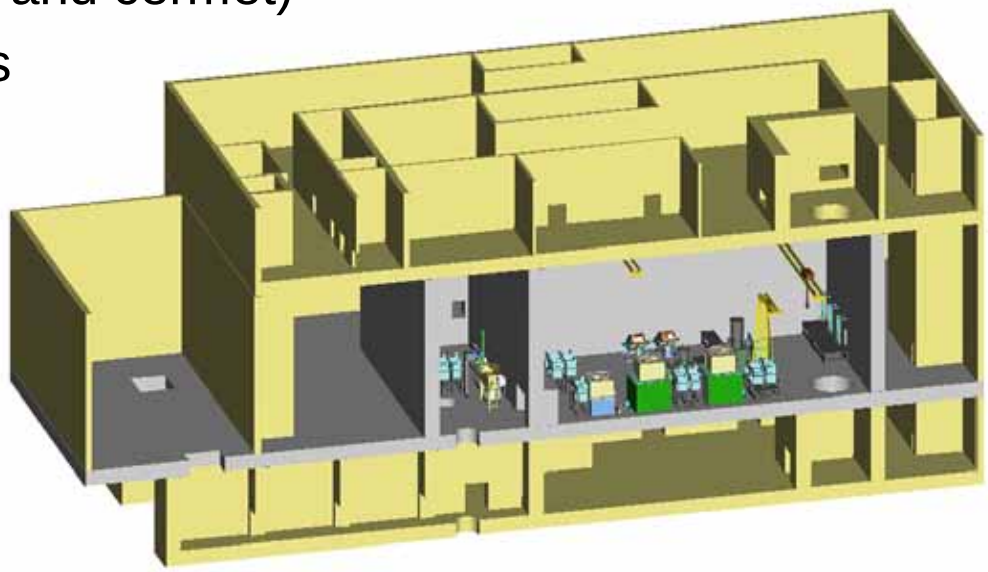
- **Develop a process flowsheet for an integrated pyroprocess oxide-fuel recycle facility**
  - Reference-case throughput of 100 tonne/yr of initial heavy metal
- **Prepare overall requirements to encompass:**
  - Individual operations
  - Facility layout
  - Mechanical and electrical equipment design
  - Maintenance and safeguarding
- **Generate conceptual designs of the facility and the individual pieces of equipment**

Process Modeling

- **Optimize facility using the operations model**
  - Evaluate equipment layout to minimize materials transfer, to simplify access to services, and to optimize equipment spacing
  - Verify facility design for throughput requirements
  - Identify design shortcomings
  - Provide efficiency data on resources
  - Determine operational bottlenecks
  - Test proposed changes for effectiveness
  - Provide equipment utilization data
- **Assess moving from batch operations to semi-continuous operations**
- **Develop an operations model of the facility**
- **Specify control interface requirements**

Process Demonstration - PYROX

- **Process for the treatment of spent light water reactor fuels to recover actinides**
  - Recycle in advanced nuclear reactors
  - Stabilize fission products for repository storage
- **Flowsheets and proof-of-concept tests for treatment of**
  - Dispersion fuels (cercer and cermet)
  - Carbide and nitride fuels
  - Particle fuels



3-D Schematic of PYROX Facility

Other ANL Capabilities Related to the Fuel Cycle

ANL Capabilities Related to the Fuel Cycle

- **Separations**
- **Repository testing and modeling**
- **Materials engineering**
- **Domestic nuclear event attribution**
- **Hydrogen production**